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AFML-TR-67-261 PART II

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**SYNTHESIS AND CHARACTERIZATION OF
PERFLUOROALKYL HETEROCYCLIC ELASTOMERS**

N.L. Madison
C.D. Burton
The Dow Chemical Company

TECHNICAL REPORT AFML-TR-67-261, PART II

December 1968

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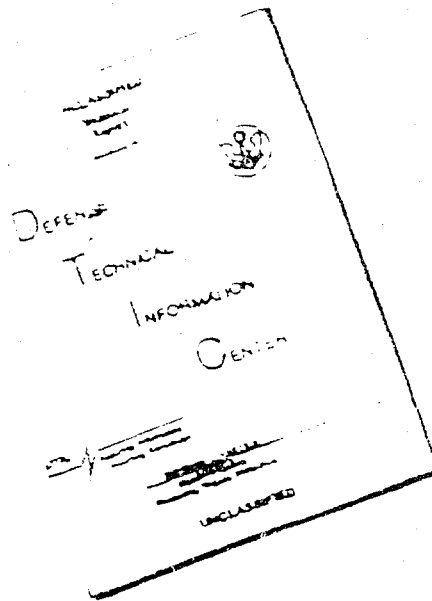
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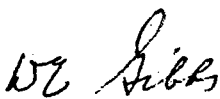
FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, on Air Force Contract Nr. AF 33(615) - 5268. The contract was initiated under Project Number 7340, Task Nr. 734004, "Synthesis and Characterization of Perfluoroalkyl Heterocyclic Elastomers." This work was sponsored and administered by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Fred E. Arnold, MANP, as Project Engineer.

This report represents the work performed on this contract for the period 1 May 1967 to 31 August 1968, and is being submitted by the authors in August, 1968. It is Dow Report Nr. PH-3Q-68. The manuscript was released by the authors November, 1968 for publication.

Management direction at Dow was under Dr. D. A. Rausch, Assistant Laboratory Director of the Chemicals Laboratory. Dr. N. L. Madison and Mr. C. D. Burton are the principal investigators, and were assisted by Mr. L. M. Bragiel.

This technical report has been reviewed and is approved.



W. E. Gibbs
Chief, Polymer Branch
Nonmetallic Materials
Division

ABSTRACT

Perfluoroalkyl bibenzoxazole polymers containing a $(CF_2)_8$ between heterocyclic rings have been prepared by the reaction of dihydroxybenzidine and methyl perfluorosebacimide. Through preparation of this polymer, the basic polymerization system has been significantly improved and polymers with number average molecular weights as high as 20,400 have been obtained in good yield and purity. These materials are thermally stable to $\sim 500^\circ C$. (TGA). Copolymers of dihydroxybenzidine and methyl perfluoro-4,-9,14,19-tetraoxadocosanediimide, which are tacky and resilient, have been prepared by the same basic reaction. Number average molecular weights of $\sim 11,500$ have been achieved, but the polymer molecular weights have not been optimized. Thermal stability is comparable to the sebacimide polymer.

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TABLE OF CONTENTS

I.	INTRODUCTION	1
II.	DISCUSSION	4
	BIBENZOXAZOLE POLYMERS FROM METHYL PERFLUOROSEBACIMIDATE	4
	PREPARATION OF PERFLUORO-4,9,14,19-TETRAOXADOCOSANE- DIIMIDATE-DIHYDROXYBENZIDINE COPOLYMERS	11
	PROPERTIES OF PERFLUORO-4,9,14,19-TETRAOXADOCOSANE- DIIMIDATE-DIHYDROXYBENZIDINE COPOLYMERS	13
	PREPARATION AND REACTIVITY OF TRIFLUOROMETHYL PERFLUOROBUTYRIMIDATE	13
	PREPARATION AND REACTIVITY OF ETHYL PERFLUOROBUTYRTHIOIMIDATE	14
III.	SUMMARY	15
IV.	EXPERIMENTAL	16
	PREPARATION OF INTERMEDIATES	16
	PREPARATION OF POLYMERS	18
	PREPARATION OF MODEL I FROM ETHYL PERFLUOROBUTYRTHIOIMIDATE	22
V.	APPENDIX	23

LIST OF ILLUSTRATIONS

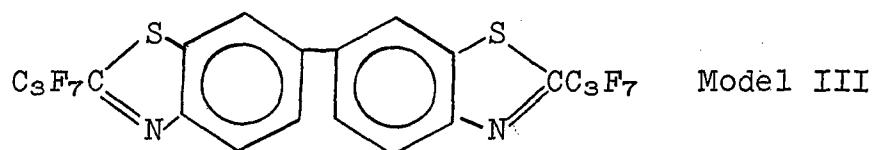
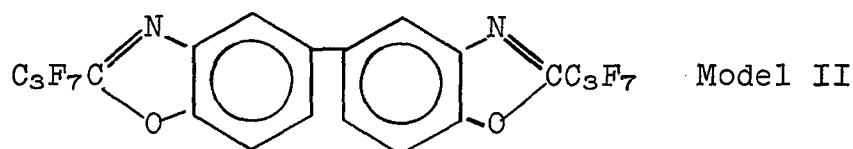
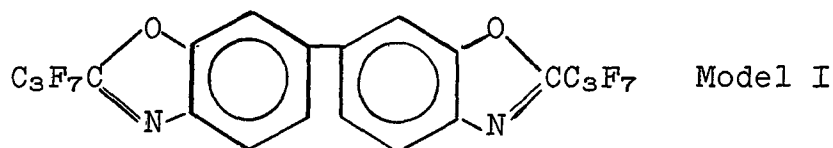
Figure 1 - TGA of Polymer 71 in Air and in Nitrogen Atmospheres	24
2 - TGA of Polymers 61H and 65H in Air and in Nitrogen Atmospheres	25
3 - TGA of Polymer 57H in Air	26
4 - DTA of Polymer 119 in Air	27
5 - DTA of Polymer 119H in Air	28
6 - Infrared Spectrum of Dimethyl Perfluoro-4,9,14,19-Tetraoxadocosanediimide	29
7 - Infrared Spectrum of Trifluoroethyl Perfluorobutyrimide	30
8 - Infrared Spectrum of Ethyl Perfluorobutyrylthioimide	31
9 - Infrared Spectrum of Perfluorosebacimide - Dihydroxybenzidine Copolymer Film	32
10 - Infrared Spectrum of Perfluoro-4,9,14-19-Tetraoxadocosanediimide-Dihydroxybenzidine Copolymer	33

SECTION I

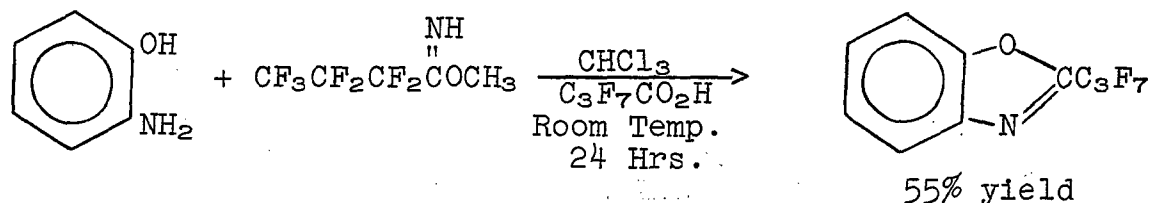
INTRODUCTION

The purpose of this research program is to synthesize heterocyclic fluorine-containing polymers for use as high temperature elastomers. Specifically, the program involves the synthesis of selected perfluoroalkyl heterocyclic model compounds and the determination of their relative stabilities followed by the synthesis and evaluation of polymers congeneric with the most attractive of these models.

Six heterocyclic systems were prepared, and the approach was to prepare model compounds of two or three of the systems for evaluation. Two bibenzoxazoles and one bibenzothiazole were selected as the initial systems and the following three models were studied:



Initially, model compounds I and II were prepared by a two-step process culminated by cyclodehydration of an intermediate bisanilide. However, yields were only 50-70% and the only effective purification was by sublimation, a process not adaptable to polymers. The preparation of these models by the Braz¹ synthesis, shown below, of benzoxazoles from aminophenols and imidate esters, was attempted.



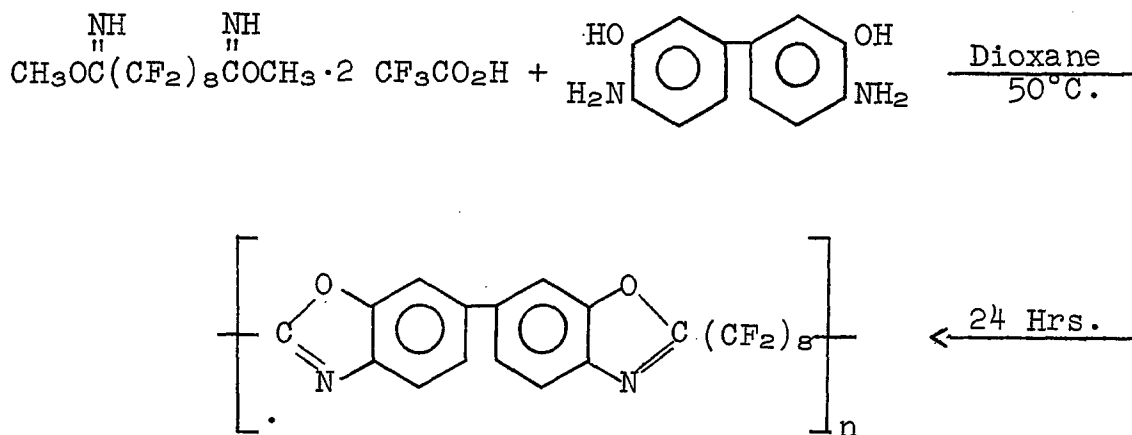
¹G. I. Braz, G. V. Myasnikova, and A. Ya. Yakubovich, Chem. Heterocyclic Compounds (English Translation), 1, 102 (1965).

Although the yields were not sufficiently high to apply the reaction to condensation polymerization, with modification, a one-step procedure for making either models or polymers in high yield was achieved. For example, when dioxane was used as the solvent and the reaction was carried out at 60°-80°C. with dihydroxybenzidine, a crude yield of nearly pure Model I in greater than 90% was obtained. In addition, it was found that trifluoroacetic acid would promote the reaction equally as well as perfluorobutyric acid regardless of the imide ester employed. With this synthesis route, Model II was prepared from 3,3'-diaminobiphenol in greater than 86% yield, and Model III was obtained in 67% yield from 3,3'-dimercaptobenzidine. In later studies, the yield of Model I was increased to nearly 100% by reducing the reaction temperature to 48-59°C.

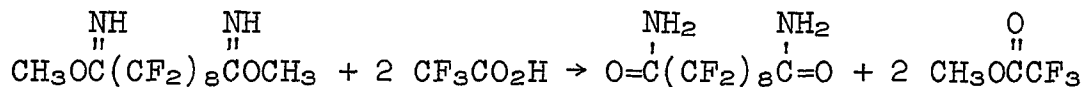
The three models were very resistant to strong acid except hot concentrated nitric acid, and were unreactive toward secondary and tertiary amines. Thermal degradation studies showed all three models were stable in the absence of air at 250°C., and Models I and III were stable at 350°C. Oxidative stability was not determined due to the volatile nature of the compounds.

These studies indicated that polymers congeneric with Models I and III would be sufficiently stable and unreactive for high temperature applications.

Polymers based on Model I were first prepared under the following conditions:



The polymer analyzed correctly for the 1:1 copolymer, but the rather brittle nature of films formed from the melt indicated that the molecular weights were low. The low molecular weights were found to be due to a side reaction of trifluoroacetic acid with the imide ester. This reaction is apparently faster with the long chain dimide than with the butyramide.



The rate of this reaction was found to be sufficiently rapid to compete with polymer formation and thereby upset the stoichiometry.

However, regardless of the promoter used, acetic acid or trifluoroacetic acid, the elemental analyses corresponded to a polymer containing a 1:1 ratio of perfluoroalkyl chain to bibenzoxazole group and the infrared analyses established that benzoxazole rings were formed.

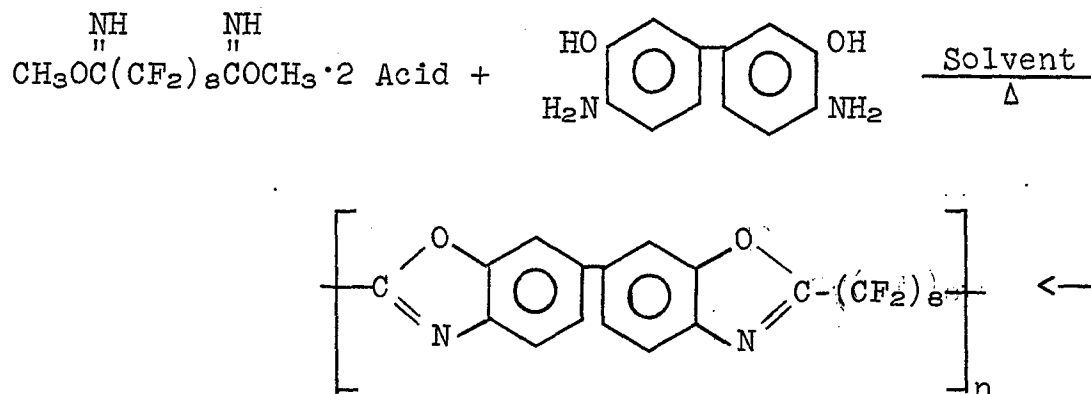
To avoid this rearrangement reaction, models and polymers were prepared in the presence of acetic acid as the promoter. With acetic acid, rearrangement did not occur and quantitative yields of polymer were obtained. However, the brittle nature of the polymers from this study indicated that the molecular weights were still low and conditions required to improve the reaction were therefore sought. A program to achieve this end was carried out in the past year and is discussed in the next section.

SECTION II

DISCUSSION

A. BIBENZOXAZOLE POLYMERS FROM METHYL PERFLUOROSEBACIMIDATE

Bibenzoxazole polymers have been prepared by the reaction of dimethyl perfluorosebacimide with dihydroxybenzidine in the presence of an acid and a solvent.



1. Promoter-Solvent Systems

In the first year of this program, polymers were prepared in a trifluoroacetic acid-dioxane system or with acetic acid as both the acid and solvent. However, these are heterogeneous systems and have not produced high molecular weights. Therefore, two solvents, hexamethylphosphoramide and hexafluoroisopropanol, which were good solvents for the early polymers, were used as reaction media.

Hexamethylphosphoramide, an effective solvent for both dihydroxybenzidine and the polymer, was used in combination with acetic acid to produce a completely homogeneous reaction. However, phosphorus in some form was incorporated into the polymer and the analysis for the other elements present was poor. In addition, since the infrared spectrum was entirely different from the previous bibenzoxazole polymers, no further reactions were carried out in hexamethylphosphoramide.

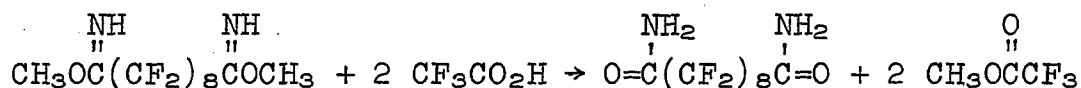
The preparation of bibenzoxazole polymers in a trifluoroacetic acid-hexafluoroisopropanol system resulted primarily in the formation of dihydroxybenzidine bis(trifluoroacetate), although a small amount of bibenzoxazole polymer was found and identified by infrared analysis. With acetic acid-hexafluoroisopropanol, a good yield of light-colored polymer was obtained. This reaction system was initially heterogeneous due to the insolubility of dihydroxybenzidine, but as this material was gradually incorporated into the polymer, a homogeneous solution was formed. The time required to reach homogeneity (about 2 days)

indicated this was a rather slow reaction, and to increase the extent of condensation the reaction time was increased from 2 to 5 days. In contrast to the previous polymers, films of this material were flexible rather than brittle indicating the molecular weight might be higher. However, ebulliometric molecular weight values for polymers prepared by the three promoter-solvent systems, (1) acetic acid-acetic acid, (2) trifluoroacetic acid-dioxane, and (3) acetic acid-hexafluoroisopropanol, were all rather low, and there was no clear-cut advantage to any one of the systems.

Since ebulliometric values are greatly influenced by small amounts of low molecular weight materials, a number of these values were redetermined by membrane osmometry. The results are shown in Table I.

The osmotic pressure molecular weight values were higher than those obtained by ebulliometry, indicating that low molecular weight material was present. Polymers prepared with acetic acid as both promoter and solvent had lower molecular weights than polymers prepared by the other two systems; therefore, this system was dropped from further consideration.

The two polymers, which were prepared with trifluoroacetic acid as the promoter and dioxane as the solvent, had different properties. When the polymerization was carried out with stoichiometric quantities of the imidate ester and dihydroxybenzidine, the polymer was insoluble in hexafluoroisopropanol, and its molecular weight could not be determined. The insolubility suggests that the material is a very low molecular weight polymer with a preponderance of polar end groups and probably terminated with the dihydroxybenzidine moiety which is known to be insoluble in hexafluoroisopropanol. The other polymer prepared in the trifluoroacetic acid-dioxane system had a moderately high molecular weight, but the reaction was carried out with a 15% excess of the imidate ester. Both of these polymerizations were subject to the previously indicated side reaction,



which would reduce the amount of imidate ester available for the polymerization. Since a condensation polymerization requires very accurate stoichiometry to attain high molecular weights, the latter reaction made the trifluoroacetic acid-dioxane system unacceptable and further development was restricted to the acetic acid-hexafluoroisopropanol system.

2. Molecular Weight Improvement

Although the copolymers of dihydroxybenzidine and methyl perfluorosebacimide melt too high (235-240°C.) for possible

Table I

Molecular Weight Values of Polymers by Ebulliometry and Osmometry

<u>Polymer</u>	<u>Method of Preparation^a</u>	<u>Molecular Weight</u>		<u>Remarks</u>
		<u>Ebulliometry</u>	<u>Osmometry</u>	
61H	1	3,030	4,320	
65H	1	2,250	---	
46H	2	Insoluble in hexafluoroisopropanol		
71H	2	7,700	11,100	Prepared with 15% excess methyl perfluorosebacimide
42H	3	2,300	9,090	
45H	3	5,900	7,350	Prepared with reprecipitated dihydroxybenzidine
45R	3	---	8,920	45H reprecipitated 3 times from hexafluoroisopropanol
54	3	---	4,160	Prepared at 113-125°C.
57H	3	---	18,000	Prepared with ultrapure dihydroxybenzidine, acetic acid and hexafluoroisopropanol

^aFor method, see text.

use in elastomeric applications, the ready availability of the monomers afforded an opportunity to optimize the acetic acid-hexafluoroisopropanol system before committing more sophisticated and expensive reactants. The early polymers, when prepared in acetic acid-hexafluoroisopropanol, were light colored and appeared to have high purity by infrared and elemental analyses, but the molecular weights were too low for a good condensation polymer.

One attempt was made to upgrade a polymer by repeated fractional precipitation from hexafluoroisopropanol using acetone, methanol, and water as the precipitating agents. Although the molecular weight of the product was increased, the improvement was not significant. In order to force the polymerization, another polymer was synthesized in a pressure reactor at 113-125°C., but the molecular weight was low and only 60% of the dihydroxybenzidine reacted, presumably due to decomposition of the imide ester at the higher reaction temperature.

a. Effect of Reactant Purity

The most significant variables were found to be those involving the purity of reactants and, concomitantly, the stoichiometry. It was noted in the early reactions that if the dihydroxybenzidine was not highly purified, a small amount of black insoluble tar formed in the final hexafluoroisopropanol solution of the polymer. Although the tar could be removed by filtration prior to precipitation of the polymer with water, the stoichiometry was adversely affected by the presence of an impurity. The dihydroxybenzidine could be prepurified by precipitation with water from a filtered hexamethylphosphoramide solution, but the color of the dried product indicated that purification was not complete.

Ultrapure dihydroxybenzidine was finally obtained by exhaustive charcoal treatment of an aqueous solution of dihydroxybenzidine dihydrochloride, followed by precipitation and isolation of the dihydroxybenzidine by techniques which minimized exposure to light and air. Dry ultrapure dihydroxybenzidine appears to be stable to storage only as long as light and air are excluded.

In order to circumvent the sensitivity during polymerization of the dihydroxybenzidine, some of which remains unreacted for as long as 48 hours, several refinements were made in the reaction conditions. Methyl perfluorosebacimide and dihydroxybenzidine were accurately weighed in a dry box and a dry nitrogen atmosphere was maintained throughout the reaction. Both acetic acid and hexafluoroisopropanol were thoroughly dried and distilled before use. No attempt was made to distill the imide ester at this time, since these materials were known to be rather unstable at elevated temperatures. The polymer obtained under these conditions was a cream solid which softened at 235°C. and there was no gassing

by the melt to at least 300°C. The melt, which was more viscous than previous polymers, could be drawn into long flexible fibers or cooled to a tough, flexible, transparent yellow film. When a sample of the polymer was heated to 300°C. for 24 hours under nitrogen, the loss in weight was only 3.2% with a loss of 0.7% in the last 20 hours. With the same treatment in air, the sample had lost 5.5% of its weight after 24 hours, but after four hours the weight loss was no greater than in nitrogen, 2.5%. The TGA decomposition point in air was 492°C. (Figure 3). The molecular weight, as measured by membrane osmometry, was 18,000.

Later, polymers were again prepared in the presence of acetic acid which had been purified by distillation from an acetic acid-acetic anhydride mixture, but the conversion of dihydroxybenzidine to polymer was incomplete and analyses of the products were poor. Investigation of the ingredients used in the reactions revealed that the acetic acid still contained some acetic anhydride which was terminating the chains or decomposing the reactants. However, when the polymerization reactions were carried out with ACS grade glacial acetic acid, dihydroxybenzidine was completely converted to high molecular weight polymers without difficulty.

Purification of methyl perfluorosebacimide was accomplished by fractional distillation under high vacuum. The main fraction distilled at 68°C./0.5 μ , after about 20% of the material was collected as a forerun which was primarily methyl perfluorosebacimide. There was no evidence of decomposition during the distillation.

Several polymerizations were subsequently carried out with distilled, center-cut methyl perfluorosebacimide, ultrapure dihydroxybenzidine, dry, distilled hexafluoroisopropanol, and ACS grade glacial acetic acid. All of the polymers were light colored solids with number average molecular weight values in the 15,000-20,000 range. (Table II).

b. Other Factors

The reaction time for the latter polymers was increased to 7 days to insure complete reaction. However, to accurately determine the effect of reaction time on molecular weights a kinetic study of the reaction under the best conditions was carried out and samples were removed over a period of five weeks. Molecular weights on the isolated polymer samples were determined by osmotic pressure measurements. The results are shown in Table III. The data appear to indicate that the ultimate molecular weight is attained shortly after the dihydroxybenzidine has dissolved and that continued heating is of no benefit. Therefore, the polymer may grow by reaction of the individual chains alternately with the two monomers rather than by combination of short chains. This would suggest that the polymerization is similar to an interfacial polymerization, except that the interface is between

an insoluble solid and a solution rather than between two immiscible liquids. If this is the case, high molecular weights should be attainable with an excess of dihydroxybenzidine.

Table II

Polymer Molecular Weights and Viscosities

<u>Polymer</u>	<u>Mol. Wt. Ebulliometry</u>	<u>Mol. Wt. Osmometry</u>	<u>Inherent Viscosity</u>	<u>Melt Viscosity poise</u>
65H	2,250	---	---	---
61H	3,030	4,320	---	9.6
45H	5,900	7,350	0.257	---
42H	2,300	9,090	0.422	---
71H	7,700	11,100	0.156	250,000
86H	---	13,100	0.345	2,240
97H	---	14,600	0.238	---
57H	---	18,000	0.472	110,000
94H	---	18,600	0.581	156,000
78H	---	20,400	0.856	2,140,000

Table III

Polymerization Kinetic Study

<u>Sample</u>	<u>Reaction Time</u>	<u>Mole. Wt.</u>	<u>Inherent Visc.</u>
104-1H	67 hrs.	15,400 (20,300) ^a	0.810
104-2H	115 hrs.	16,700 (28,000) ^a	0.734
104-3H	1 wk.	15,900 (9,300) ^a	0.806
104-4H	2 wk.	15,900	0.659
104-5H	3 wk.	15,800	--
104-6H	4 wk.	14,700	--
106-7H	5 wk.	13,800	--
10295-57H ^b	115 hrs.	18,000	0.472

^aMolecular weights determined at an earlier date.

^bPolymer prepared with undistilled imidate.

Although the evidence points to essentially no change in the molecular weight of the last sample from the first, the physical appearance of the polymer samples differ. When precipitated with methanol, the first sample emerged rather slowly and dried to a powder, whereas the latter samples precipitated instantly and had the "stringy" appearance more characteristic of higher molecular weight polymer.

When the study was initiated, it was proposed to compare sample 104-2H with 10295-57H. Both materials were prepared under identical conditions except that undistilled imidate was used in 10295-57H. Unfortunately, the molecular weights were not sufficiently reliable to determine a trend, although the infrared spectra did indicate that 10295-57H contained more of the bands attributed to acid or amide groups.

The molecular weight determinations for the first three samples are indicative of the rather poor reproducibility that has been encountered with hexafluoroisopropanol solutions. Even the inherent viscosities, also measured in hexafluoroisopropanol, have sufficient variance to cast some doubt on the validity of the values. The values for both the molecular weights and inherent viscosities tend to diminish for the later samples and it seems quite unlikely under the reaction conditions that depolymerization should occur.

As measured in hexafluoroisopropanol, molecular weight and inherent viscosity values do not properly correlate. For those selected polymers which show correlation in the right direction, the rate of viscosity change with molecular weight is too high. This could indicate hexafluoroisopropanol is a poor theta solvent or small amounts of gel may be present in the solution.

To determine if some gel, due to crosslinking, might be present in the hexafluoroisopropanol solutions, 104-5H was submitted for light scattering studies. Although no gel was detected on the "frit", the solution was difficult to filter and moderate distortion of the Zimm plot indicated "some gel might be present." To further investigate if gels might be formed during past polymerization heat treatment, polymer was prepared in the usual manner and purified by repeated reprecipitation from hexafluoroisopropanol rather than by heat. Heated and unheated samples of this polymer were subjected to differential thermal analysis to see if a crosslinking reaction could be detected. The DTA curves of the two materials are shown in Figures 4 and 5. There is a small unexplained exotherm at 110°C. in the unheated sample (Figure 4), but this temperature change is too small to be indicative of a crosslinking reaction. Since the polymers are still completely soluble in sulfuric acid, it has not been conclusively determined whether the polymers, as prepared, are crosslinked or whether molecular weights are sufficiently high to be only partially soluble in hexafluoroisopropanol. The weight average molecular weight by light scattering was about 126,000.

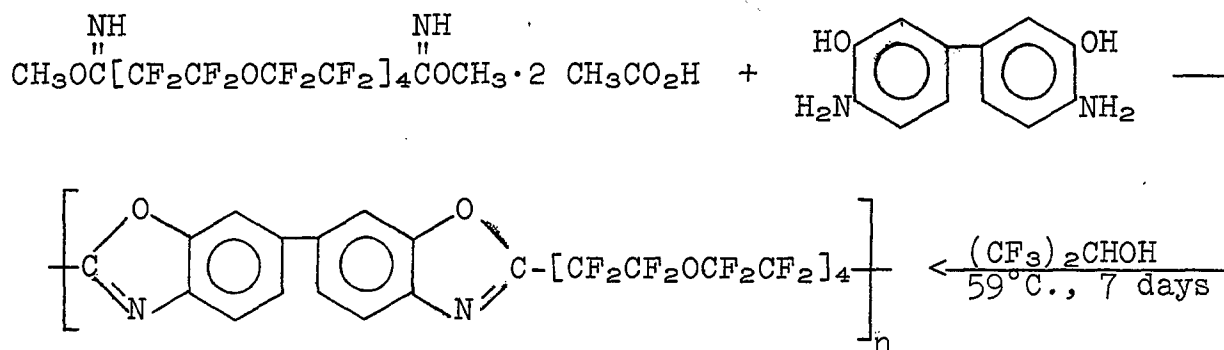
Some crosslinking can be accomplished by heating the polymer near its melting point for 1-2 hours. The resulting material is only semi-fusible to 350°C. and completely insoluble in hexafluoroisopropanol and concentrated sulfuric acid. However, the flexible nature of the product indicates crosslinking is very limited and may be due to imperfect sites in the polymer. Pure Model I heated to 350°C. showed a tendency to resinify.

3. Polymer Properties

The bibenzoxazole polymers are light colored solids which melt at ~240°C. and both films and fibers can be obtained from the melt. With higher molecular weight materials, films can be cast from hexafluoroisopropanol solutions. They are soluble only in hexafluoroisopropanol and sulfuric acid although the lower molecular weight polymers are also soluble in hexamethylphosphoramide. Elemental analysis of polymers prepared in dioxane, acetic acid, or hexafluoroisopropanol are close to theoretical and gave no indication of the end groups present. Infrared studies have shown trace amounts of some extraneous functions, primarily carbonyl, which are probably associated with the terminal groups. Heating the polymers under vacuum to 205°C. reduces these functions slightly. NMR studies are not conclusive, but the presence of a methyl ester at the terminus is indicated and such a terminal group is consistent with infrared data. The source of this group is probably from hydrolysis of terminated methylperfluoroimide during work-up. The polymers are stable in air (TGA) (Figure 3) to ~500°C., and their films, cast from hexafluoroisopropanol, do not lose their flexibility when heated at 200°C. for 21 hours. By DTA, the polymers show only an endotherm at the melting point and there is no indication of a glass transition temperature. The small exotherm at 110°C. disappears after the first heating and, therefore, cannot be the Tg (Figure 4). The endotherm just before the melting point is probably an artifact caused by shrinkage of the polymer away from the thermocouple during the melting process.

B. PREPARATION OF PERFLUORO-4,9,14,19-TETRAOXADOCOSANEDIIMIDE-DIHYDROXYBENZIDINE COPOLYMERS

Although the perfluorosebacimide-dihydroxybenzidine polymers have excellent thermal properties, they are not elastomers. To improve the polymer flexibility and thereby enhance the chances of obtaining elastomeric properties, the longer chain perfluoro-alkyl imide, methyl perfluoro-4,9,14,19-tetraoxadocosanedimide, was reacted with dihydroxybenzidine in the following manner:



Ultrapure dihydroxybenzidine, dry distilled hexafluoroisopropanol, and ACS grade glacial acetic acid were used in the reaction. The imide was prepared from the dinitrile in the usual way and the excess alcohol and catalyst were removed under high vacuum. The yellow imide which contained a small amount of white solids was filtered, but no attempt was made at further purification. The infrared spectrum of the imide was compatible with the proposed structure and very similar to the spectrum of distilled methyl perfluorosebacimide.

The reaction characteristics were very similar to the perfluorosebacimide-dihydroxybenzidine polymerizations, i.e., the dihydroxybenzidine completely dissolved in 48 hours and the clear yellow solution did not change in the last 5 days. The polymer did not fully precipitate when the reaction mixture was poured into methanol and it was necessary to strip the solvents to completely isolate the product. This is not a good procedure since by-product ammonium acetate is not removed. The polymer was purified by heating to 205°C. under high vacuum (1 μ) for two hours. A small amount of material sublimed from the bottom of the tube and condensed in two rings around the top of the tube. By infrared analysis, the upper ring appeared to be fairly pure low molecular weight polymer and the lower ring contained bands characteristic of polymer contaminated with what appeared to be carboxyl or amide functions.

These by-product, which comprised about 15% of the yield, were not completely removed by sublimation. The polymer can be further purified by exhaustive washing with methylene chloride or acetone, but in no case was the by-product, as detected by infrared spectroscopy, completely removed, indicating the rest of the acid or amide moieties were probably end-groups or the result of incomplete cyclization. The residue which was the major polymer fraction also contained carboxyl or amide functions (Figure 3), but to a lesser extent than the sublimate.

The purity of the polymers was dependent on the purity of the starting imidate. Polymers prepared from undistilled material exhibited a rather large infrared band at 5.8-5.9 μ and a broad absorption at 2.9-3.4 μ , while with distilled imidate the bands were considerably smaller. Methyl perfluoro-4,9,14,19-tetraoxadocosane-diimidate distilled over a rather wide range, 96-104°C. at 1 μ ,

but, by fractional distillation, the range was reduced to 90-93°C. at 0.5 μ . The same impurities determined by infrared analysis in the polymers were also detected in the forerun and residue of this distillation. Although the purity of the center-cut imide ester appeared to be high, fractionation was not very efficient due to the small size of the sample. A narrower range should be attainable on a larger scale. Polymer prepared from center-cut imide contained less impurity than any of the polymers prepared. However, the molecular weights of polymers prepared from fractionally distilled and undistilled imide were essentially the same, 11,400-11,600.

C. PROPERTIES OF PERFLUORO-4,9,14,19-TETRAOXADOCOSANEDIIMIDATE-DIHYDROXYBENZIDINE COPOLYMERS

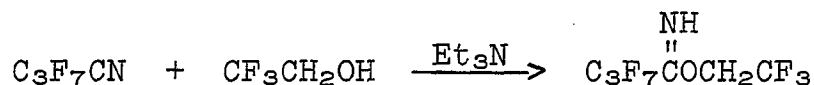
The perfluoro-4,9,14,19-tetraoxadocosanediimide-dihydroxybenzidine copolymers are tacky, resilient materials with only a slight tendency to flow at room temperature. At -30°C., the polymer becomes hard but not brittle. It is insoluble in ordinary solvents, very slightly soluble in concentrated sulfuric acid, and completely soluble only in hexafluoroisopropanol. When heated under vacuum at 240°C., the viscous melt bubbles, but no volatile products have been detected.

After bubbling ceases (about 2 hours), the polymer, which no longer flows, is a rubbery elastomer which retains its properties when heated to 300°C. The elastomer is insoluble in sulfuric acid and hexafluoroisopropanol, although it tends to break up in the latter solvent. Elemental analysis indicates the elastomer may have a lower fluorine content than its precursor polymer. Since a brittle material is not formed, the crosslinking is probably occurring at imperfect sites in the polymer.

The heat stability of the dihydroxybenzidine-methyl perfluoro-4,9,14,19-tetraoxadocosanediimide copolymer is comparable to the dihydroxybenzidine-methyl perfluorosebacimide copolymers.

D. PREPARATION AND REACTIVITY OF TRIFLUOROMETHYL PERFLUOROBUTYRIMIDE

The reactivity of the methyl perfluoroalkylimide esters has been attributed to the presence of the electronegative perfluoroalkyl group. When the alkoxy groups also contained fluorine, the two electron withdrawing groups were expected to enhance reactivity and polymerization, thereby eliminating the need for an acid promoter. Therefore, trifluoroethyl perfluorobutyrimide, which was prepared by the following reaction, was investigated.



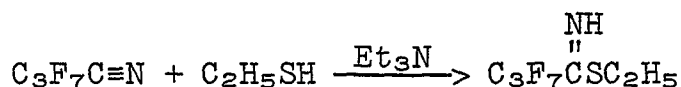
The activity of this imide ester was not sufficient to carry out the formation of Model I in the absence of an acid promoter

and the reaction rate in the presence of acetic acid was no greater than with methyl perfluorobutyrimide. Trifluoroethyl perfluorobutyrimide reacts with trifluoroacetic acid to form perfluorobutyramide, although the reaction is slower than with the methyl perfluoroimides.

E. PREPARATION AND REACTIVITY OF ETHYL PERFLUOROBUTYRTHIOIMIDATE

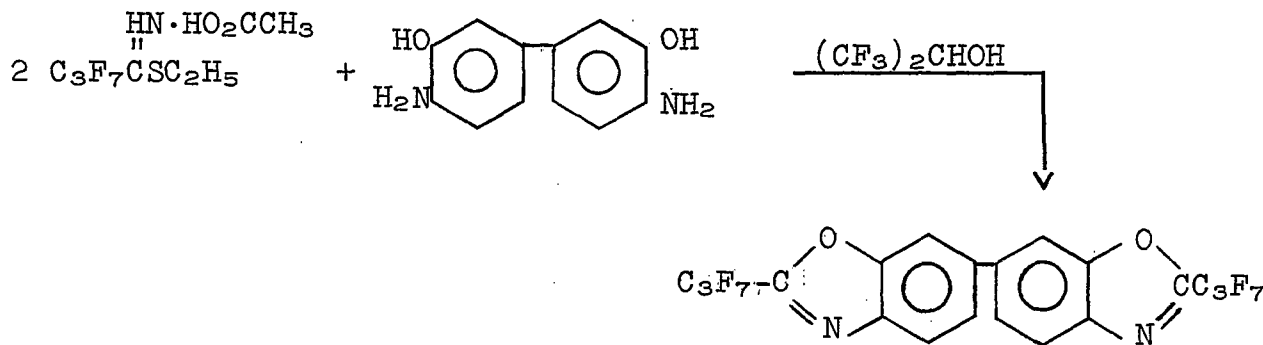
It has been reported that the salts formed by thioimides and strong acids do not rearrange to thioamides. Therefore, if thioimides could be substituted for imides in the polymerization reaction, a stronger acid promoter could be used to increase the rate of polymerization.

Ethyl perfluorobutyrrthioimide was prepared by the following reaction:



The experimental procedure was the same used for the preparation of methyl perfluorobutyrimide. The yield of distilled ethyl perfluorobutyrrthioimide was 94% based on perfluorobutyronitrile.

Model I was prepared from ethyl perfluorobutyrrthioimide in 98% yield using the hexafluoroisopropanol-acetic acid system.



Model I

The crude product (M.P. 146-148°C.) was much purer than that obtained from methyl perfluorobutyrimide.

Ethyl perfluorobutyrrthioimide is presently being heated in the presence of trifluoroacetic acid to determine if rearrangement to the amide occurs. No reaction occurs at room temperature.

SECTION III

SUMMARY

Copolymers of dihydroxybenzidine and methyl perfluorosebacimide have been prepared with trifluoroacetic acid-dioxane, acetic acid-acetic acid, or acetic acid-hexafluoroisopropanol as the promoter-solvent system. The best system for obtaining high molecular weight polymers is acetic acid-hexafluoroisopropanol; it has been adopted as the standard system.

Using anhydrous conditions, careful 1/1 stoichiometry, and all purified materials, bibenzoxazole polymers containing $-(CF_2)_8-$ groups between heterocyclic rings have been prepared and molecular weights (membrane) of 14,600-20,400 have been attained with consistency. These cream polymers soften at $\sim 240^\circ C$. to form viscous melts which can be formed into tough, flexible, transparent films or drawn into long flexible fibers. The polymer has been shown to be crystalline. Upon heating for 24 hours at $300^\circ C$. in nitrogen, the polymer loses only 3.2% of its weight, while under the same conditions in air, the weight loss is 5.5%. The TGA decomposition point in air is $\sim 500^\circ C$. and no glass transition point has been detected by DTA.

A second copolymer has been prepared by the reaction of dihydroxybenzidine with methyl perfluoro-4,9,14,19-tetraoxadocosanediimide. These polymers, which contain the $(CF_2CF_2OCF_2CF_2)_4$ group between heterocyclic rings, are tacky and resilient. Polymers from distilled imide contain less acid and amide functions than polymers prepared from crude imide, but the molecular weights, 11,400-11,600, are essentially the same. When heated to $240^\circ C$. for two hours, elastomers are formed which retain their elastomeric properties to at least $300^\circ C$. Since the heated samples do not become hard and brittle, crosslinking must be limited, probably to imperfect sites on the polymer. Optimization of the reaction, involving primarily purification of the imide, is not complete. The thermal stability of the polymer (TGA) is about the same as the sebacimide polymer.

Ethyl perfluorobutyrylthioimide reacts with dihydroxybenzidine to give excellent yields of Model I. Difunctional perfluoroalkylthioimides, in the form of their trifluoroacetic acid salts, will be reacted with dihydroxybenzidine in an attempt to increase the rate of the polymerization reaction.

SECTION IV

EXPERIMENTAL

A. PREPARATION OF INTERMEDIATES

1. Purification of Dihydroxybenzidine

Dihydroxybenzidine dihydrochloride was prepared by reacting o-anisidine dihydrochloride, 58.4 g., with aluminum chloride, 124 g., suspended in 300 ml. of toluene. After decanting off the toluene, the solids were poured into a beaker containing 150 g. of ice and 150 ml. of concentrated hydrochloric acid. The slurry of dihydroxybenzidine dihydrochloride was separated in two loads on a 5" basket centrifuge and vacuum dried at 50°C. The dry dihydrochloride was dissolved in water and filtered by suction to remove a small amount of black tar. Norit charcoal, 2 g., was added to the filtrate and after 30 minutes, the charcoal was removed by filtration. The filtrate which was still colored, was treated with Norit charcoal, 1 g., and refluxed for one hour. After filtration, the light colored solution was treated once more with Norit, 0.5 g., and refluxed for one hour. To the filtrate of this charcoal treatment was added a solution of sodium acetate, 32.8 g., in 150 ml. of water. The slurry of dihydroxybenzidine was maintained under a nitrogen atmosphere and then filtered through a "frit" with nitrogen pressure. The filter cake was washed with deionized water, ethanol and finally with anhydrous ethyl ether to displace the other washes. The dihydroxybenzidine was transferred to a 100 ml. flask covered with aluminum foil to exclude light. The flask was connected, via an adapter with stopcock, to the vacuum line and pumped to 1 μ at room temperature for 24 hours. The yield of white dihydroxybenzidine was 39.8 g. and infrared analysis indicated high purity. The material was transferred to a solvent-free nitrogen dry box and protected from exposure to light by a foil wrapping.

Analysis: Theory - C, 66.7; H, 5.57; N, 12.96

Found - C, 66.6; H, 5.46; N, 12.97

2. Distillation of Methyl Perfluorosebacimide

Methyl perfluorosebacimide was prepared and isolated in the usual way, and 40 g. of the crude material was transferred to a 25 ml. flask connected to a still head. No column was used. The still head was connected directly to the vacuum line and the equipment was evacuated. The material bubbled for a few minutes and when no more bubbles appeared, the still pot was heated with an oil bath. The following cuts were taken:

Analysis: Theory - C, 24.4; H, 1.02; F, 64.4; N, 4.75

Found - C, 24.5; H, 1.3; F, 64.4; N, 4.69

5. Preparation of Ethyl Perfluorobutyrrthioimide

Triethylamine, 0.6 ml., was placed in a 6 oz. Fischer-Porter aerosol compatibility bottle containing a magnetic stirring bar. The bottle was cooled to -196°C . and evacuated. Perfluorobutyronitrile, 21.5 g., and ethanethiol, 18.6 g., (both measured by expansion) were condensed into the bottle. The bottle was closed and allowed to warm to room temperature. The clear colorless solution was stirred overnight. The solution was transferred to a still and the excess ethanethiol as distilled at atmospheric pressure. Ethyl perfluorobutyrrthioimide was distilled under vacuum collecting the reaction boiling at $53^{\circ}\text{C}/43\text{ mm}$. $-55^{\circ}\text{C}/44\text{ mm}$. The yield was 25.47 g. (94%).

B. PREPARATION OF POLYMERS

1. Bibenzoxazole Polymer from Methyl Perfluorosebacimide in Hexamethylphosphoramide

The reaction was carried out in a 100 ml. "Mini-Lab" reactor equipped with a stirrer, thermometer, addition tube and reflux condenser. The reaction was run under a nitrogen atmosphere. Purified dihydroxybenzidine, 1.76 g., and hexamethylphosphoramide, 40 ml., were placed in the reactor and stirred until solution was complete. Methyl perfluorosebacimide, 4.2 g., glacial acetic acid, 1.0 ml., and hexamethylphosphoramide, 10 ml., were placed in the addition tube and gradually added to the reactor over a period of about 15 minutes. There was no exotherm. The stirred solution was heated to 60°C . for 114 hours during which time there was no visual change. The cooled reaction mixture was filtered to remove a trace of tars and the product was precipitated by dilution with 300 ml. of water. After filtration, the dark solid was vacuum dried overnight. The yield was 64%. The infrared spectrum was not the same as the other polymers. A small amount of the solid was heated to 205°C . (1 μ) for 2 hours. The white sublimate appeared to be an amide and the infrared spectrum of the polymer was still different than the usual polymer spectrum.

Analysis: Theory - C, 41.7; H, 0.95; N, 4.4; P, 0.0

Found - C, 38.1; H, 0.89; N, 6.47; P, 1.0

2. Bibenzoxazole Polymer from Methyl Perfluorosebacimide

The hexafluoroisopropanol, which was obtained from du Pont, was dried over magnesium sulfate and redistilled. Glacial acetic acid was treated with a small amount of acetic anhydride, stirred 24 hours and redistilled. The purity of the hexafluoroisopropanol and acetic acid was verified by V.P.C. analysis. The dihydroxybenzidine used in this reaction was the same material described in Part A.

Distilled perfluorosebacnitrile, 3.67 g., and anhydrous methanol, 25 ml., were placed in a 3 oz. Fischer-Porter reactor under a nitrogen atmosphere. The reactor was cooled to 0°C. and anhydrous triethylamine, 0.5 ml., was added with a syringe. The reaction mixture was allowed to gradually warm to room temperature and was stirred for 18 hours. The triethylamine and excess methanol were removed by vacuum at ambient temperature, having solid white methylperfluorosebacimide. The imide was pumped to 1 μ for 18 hours and transferred to a solvent-free nitrogen dry box.

In the dry box, dihydroxybenzidine, 1.42 g., was charged to the 100 ml. flask of a "Mini-Lab" reactor, equipped with a stirrer, thermometer, condenser and an addition tube. Methyl perfluorosebacimide, 3.40 g., was placed in the addition tube and the reactor was transferred to the hood. The top of the condenser was connected to a nitrogen bubbler to maintain the nitrogen atmosphere. Hexafluoroisopropanol, 50 ml., was added via syringe to the flask to give a light colored slurry. Anhydrous acetic acid, 0.75 ml., was added to the methyl perfluorosebacimide in the addition tube to form a clear colorless solution. With stirring, the imide-acid mixture was added dropwise to the flask and the tube was rinsed down with 2 ml. of hexafluoroisopropanol. The reactor was heated to the reflux temperature of hexafluoroisopropanol, 59°C. After two days, solution was nearly complete and the reaction was terminated after a total of 114 hours. The reactor was cooled and the contents of the flask were poured into 300 ml. of methanol to precipitate the polymer. The product was filtered, washed with methanol and dried under vacuum at 50°C. The yield of white polymer was 3.98 g. A sample of the polymer was heated under vacuum (1 μ) at 210-230°C. for two hours and 99% of the material was recovered.

Analysis: Theory - C, 41.7; H, 0.95; F, 47.9; N, 4.4

Found - C, 41.35; H, 1.04; F, 47.3; N, 4.46

M.P. 235°C. (viscous melt)

Inherent viscosity - 0.472 (hexafluoroisopropanol at 25°C.)

M.W. (osmometry) - 18,000

Decomposition point (TGA) - 492°C.

Isothermal TGA (300°C.)

Nitrogen 3.2% loss in weight (24 hrs.)

Air 5.5% loss in weight (24 hrs.)

3. Bibenzoxazole Polymer from Methyl Perfluorosebacimide

The reactor was a flat bottomed cylindrical glass tube (capacity about 160 ml.) tapered at the top and welded to an 8-inch small bore condenser with a female 14/20 F joint at the top. A pressure equalized addition funnel with a "Teflon" stopcock and male and female 14/35 F joints at bottom and top, respectively, was joined to the top of the reactor condenser with a "Teflon" sleeve. The top of the addition tube was connected via standard tapered joints with "Teflon" sleeves through a gas bubbler to a source of dry

nitrogen. No lubricants or greases were used. Purified dihydroxybenzidine, 1.45 g. (0.00672 mole), was charged to the reactor in a dry box. Distilled methyl perfluorosebacimide, 3.47 g. (0.00672 mole), and A.C.S. grade glacial acetic acid, 0.8 ml. (0.014 mole) were charged to the addition funnel in a dry nitrogen bag. The reactor and addition funnel were transferred to a hood and assembled while maintaining the nitrogen atmosphere. Dry distilled hexafluoroisopropanol was added by syringe, 40 ml. to the reactor and 10 ml. to the addition funnel. With stirring, the contents of the addition funnel was added dropwise to the reactor over a period of about 5 minutes. The funnel and condenser were washed down with 2-5 ml. portions of hexafluoroisopropanol and the stirred white slurry was heated to reflux (59°C.) with an oil bath. After 50 hours, the dihydroxybenzidine had dissolved leaving a clear amber solution. After heating at 59°C. for seven days and then cooling to 25°C., the solution was pressure-filtered through a "frit" and the polymer was precipitated by pouring the filtrate into 300 ml. of stirred methanol. The white polymer was isolated by vacuum filtration and washed with methanol and water. The yield after vacuum drying at 50°C. was quantitative. The dried polymer was heated to 205°C. under full vacuum (1 μ) for two hours to remove the last traces of ammonium acetate.

Analysis: Theory - C, 41.7; H, 0.95; F, 47.9; N, 4.4

Found - C, 41.55; H, 1.07; F, 46.2; N, 5.07

M.P.: 240°C. (viscous melt)

Inherent viscosity: 0.856 (hexafluoroisopropanol at 25°C.)

Melt viscosity: 2,140,000 poises (250°C.)

M.W. (osmometry) : 20,400

4. Kinetic Study of Methyl Perfluorosebacimide-Dihydroxybenzidine Copolymerization

A one piece reactor described in section B.3 above was used for this study. No greases or lubricants were used and the reaction was maintained under a nitrogen atmosphere. Purified dihydroxybenzidine, 1.91 g. (0.0088 mole), was charged to the reactor in a dry box. Distilled methyl perfluorosebacimide, 4.56 g. (0.0088 mole), and A.C.S. grade glacial acetic acid, 1.23 g. (0.020 mole), were charged to the addition funnel in a dry nitrogen bag. The reactor and addition funnel were transferred to a hood and assembled while maintaining the nitrogen atmosphere. Dry distilled hexafluoroisopropanol, 50 ml., was added via syringe to the reactor and 15 ml. to the addition funnel. With stirring, the contents of the addition funnel were added dropwise to the reactor over a period of about five minutes. The funnel and condenser were washed down with 2-5 ml. portions of hexafluoroisopropanol and the slurry was heated to reflux (58°C.) with an oil bath. The dihydroxybenzidine dissolved in approximately 60 hours leaving a clear amber solution. After 67 hours, the reactor was cooled to 50°C. and about 10 ml. of the solution were removed through the condenser with a

nitrogen-flushed pipette and bulb. The reactor was immediately reheated to reflux, and the withdrawn sample was dropped into 40 ml. of stirred methanol to precipitate the polymer. The pipette was rinsed with a few ml. of hexafluoroisopropanol which was added to the methanol. After stirring for 15 minutes, the polymer was filtered, washed with methanol and vacuum dried at 50°C. for two hours. The dried polymer was heated to 205°C. under full vacuum (1 μ) for two hours to remove the last traces of ammonium acetate. Samples were removed in a like manner after 115 hours, 1 week, 2 weeks, 3 weeks 4 weeks and 5 weeks. For the last sample the entire remaining solution was used. All seven samples were processed identically and the total yield was 94.7%. The sample removed after two weeks assayed as follows:

Analysis: Theory - C, 41.7; H, 0.95; F, 47.9; N, 4.4
 Found - C, 41.6; H, 0.89; F, 47.1; N, 5.17

Inherent viscosity: 0.659 (hexafluoroisopropanol)
 M.W. (osmometry): 15,900

5. Preparation of Bibenzoxazole Polymer from Methyl Perfluoro-4,9-14,19-tetraoxadocosanediimide, $\text{CH}_3\text{OC}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2)_4\text{COCH}_3$
 NH NH

The equipment and procedure were the same as described in Part B.3. To the reactor were charged dihydroxybenzidine, 1.145 g. (0.0053 mole), and dry hexafluoroisopropanol, 50 ml. Cut number 2 of the above distilled imide, 5.17 g. (0.0053 mole), ACS grade glacial acetic acid, 0.73 g. (0.012 mole), and dry hexafluoroisopropanol, 10 ml., were placed in the addition funnel. The equipment was assembled as before and the contents of the funnel were added dropwise over a period of about 10 minutes. The funnel and condenser were washed down with 10 ml. more hexafluoroisopropanol and the reaction was heated to reflux. After about 50 hours, solution was complete and reflux was continued for a total of 9 3/4 days. After cooling, the solution was pressure filtered through a "frit" and most of the solvent was removed by vacuum at 25°-50°C. Full vacuum (1 μ) was then applied and heat was gradually increased to 210°C. and held for three hours. During this heating period, the polymer bubbled slowly and a sublimate collected in the cool end of the tube. Both sublimate and residue were tacky and the infrared spectra were similar. The sublimate weighed 0.9 g. and the polymer weighed 4.6 g. (79% yield).

Polymer Analysis:

Theory - C, 32.8; H, 0.55; F, 55.4; N, 2.55
 Found - C, 32.65; H, 0.55; F, 54.3; N, 3.47
 Molecular Weight - 11,600

A sample of perfluoro-4,9,14,19-tetraoxodocosanediiimide dihydroxybenzidine copolymer was reheated to 240°C. for four hours and the resulting elastomeric solid did not melt at 300°C., and was insoluble in sulfuric acid or hexafluoroisopropanol.

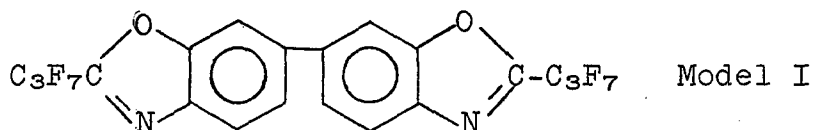
Analysis: Theory - C, 32.8; H, 0.55; F, 55.4; N, 2.55

Found - C, 34.5; H, 0.74; F, 51.3; N, 2.75

C. PREPARATION OF MODEL I FROM ETHYL PERFLUOROBUTYRTHIOIMIDATE

All equipment was predried and a nitrogen atmosphere was maintained throughout the reaction. Dihydroxybenzidine, 2.05 g. (0.0095 mole), was placed in a 6 oz. Fischer-Porter aerosol compatibility bottle in a dry box and ethyl perfluorobutyrrthioimide, 5.43 g. (0.021 mole), and ACS grade glacial acetic acid, 1.47 g. (0.0245 mole), were mixed in an addition funnel in a nitrogen dry bag.

Hexafluoroisopropanol was added, 40 ml. to the bottle and 10 ml. to the addition funnel, and the funnel was joined to the bottle with a polyethylene connection. The contents of the funnel were gradually added to the bottle and chased with 5 ml. of hexafluoroisopropanol. After removal of the funnel, the bottle was capped and transferred to an oil bath where the reaction was heated. After 17 hours the dihydroxybenzidine had dissolved and the reaction was terminated after 20 hours. The solution was pressure filtered through a "frit" and the filtrate was poured into 250 ml. of water to precipitate Model I.



The product was filtered, washed with water, and vacuum dried to a constant weight. The yield of white product was 5.32 g. (98%). The melting point was 146°-148°C. (theory 147.5-148°C.).

SECTION V

APPENDIX

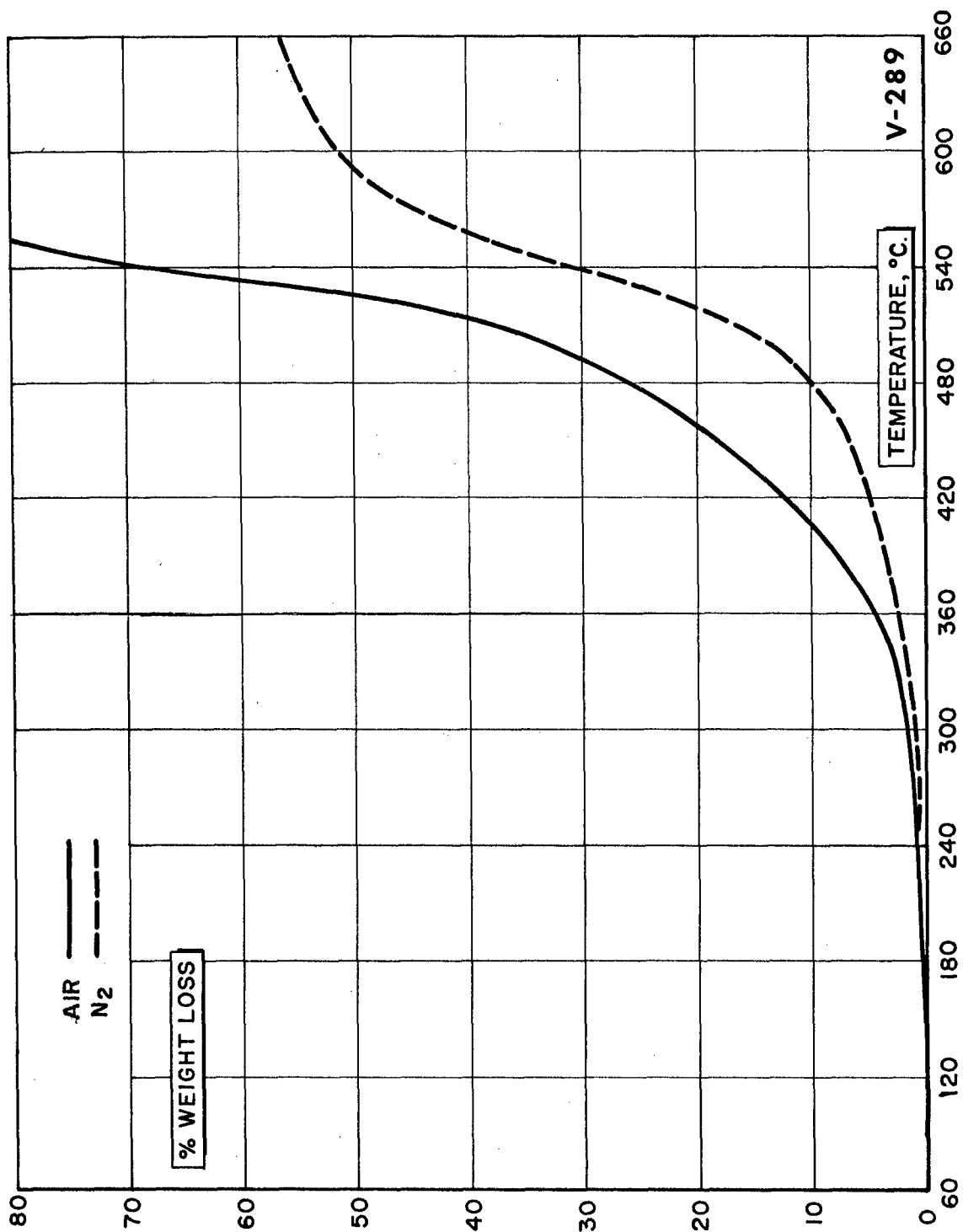


Fig. 1 - TGA of Polymer 71 in Air and in Nitrogen Atmospheres

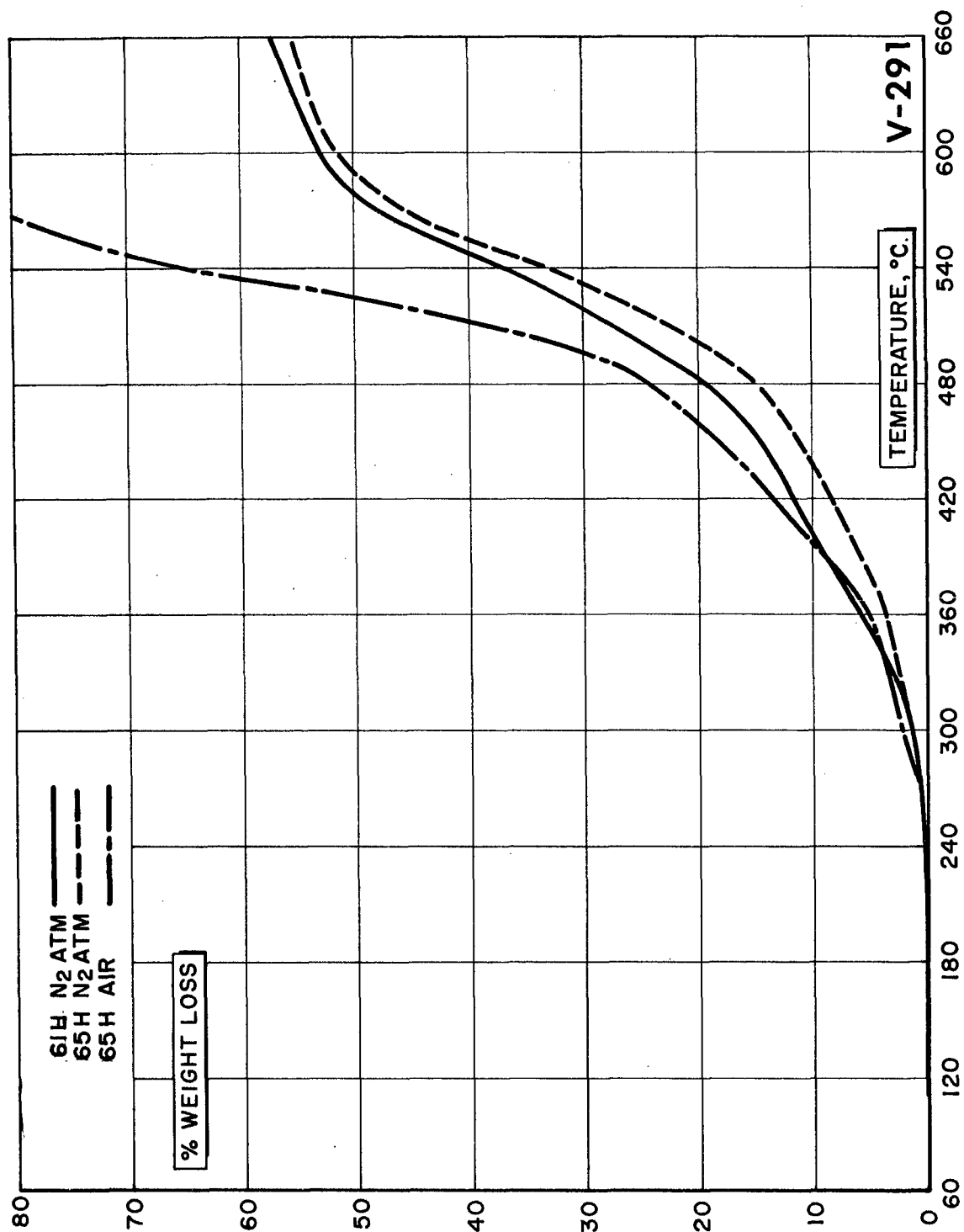


Fig. 2 - TGA of Polymers 61H and 65H in Air and in Nitrogen Atmospheres

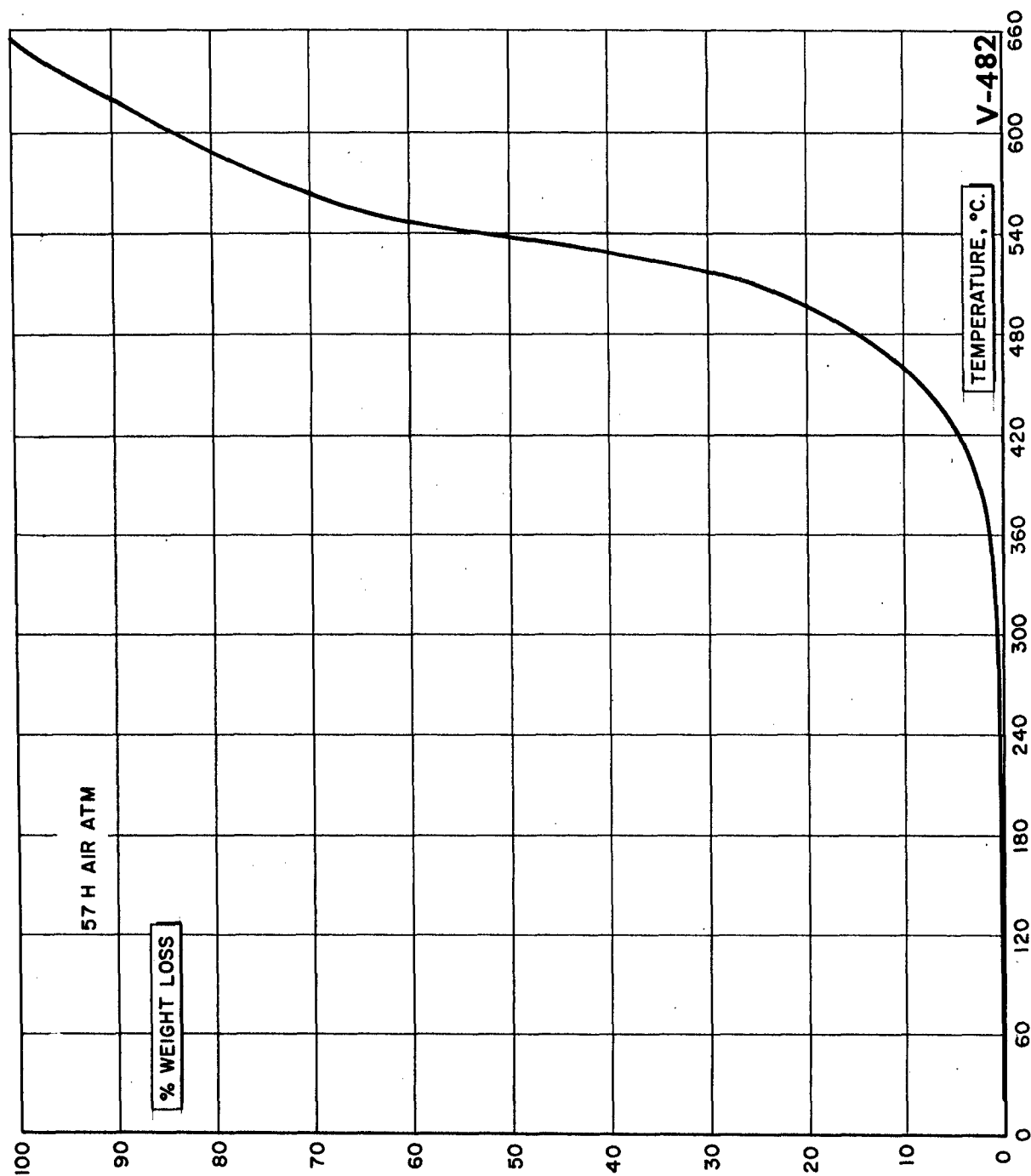


Fig. 3 - TGA of Polymer 57H in Air

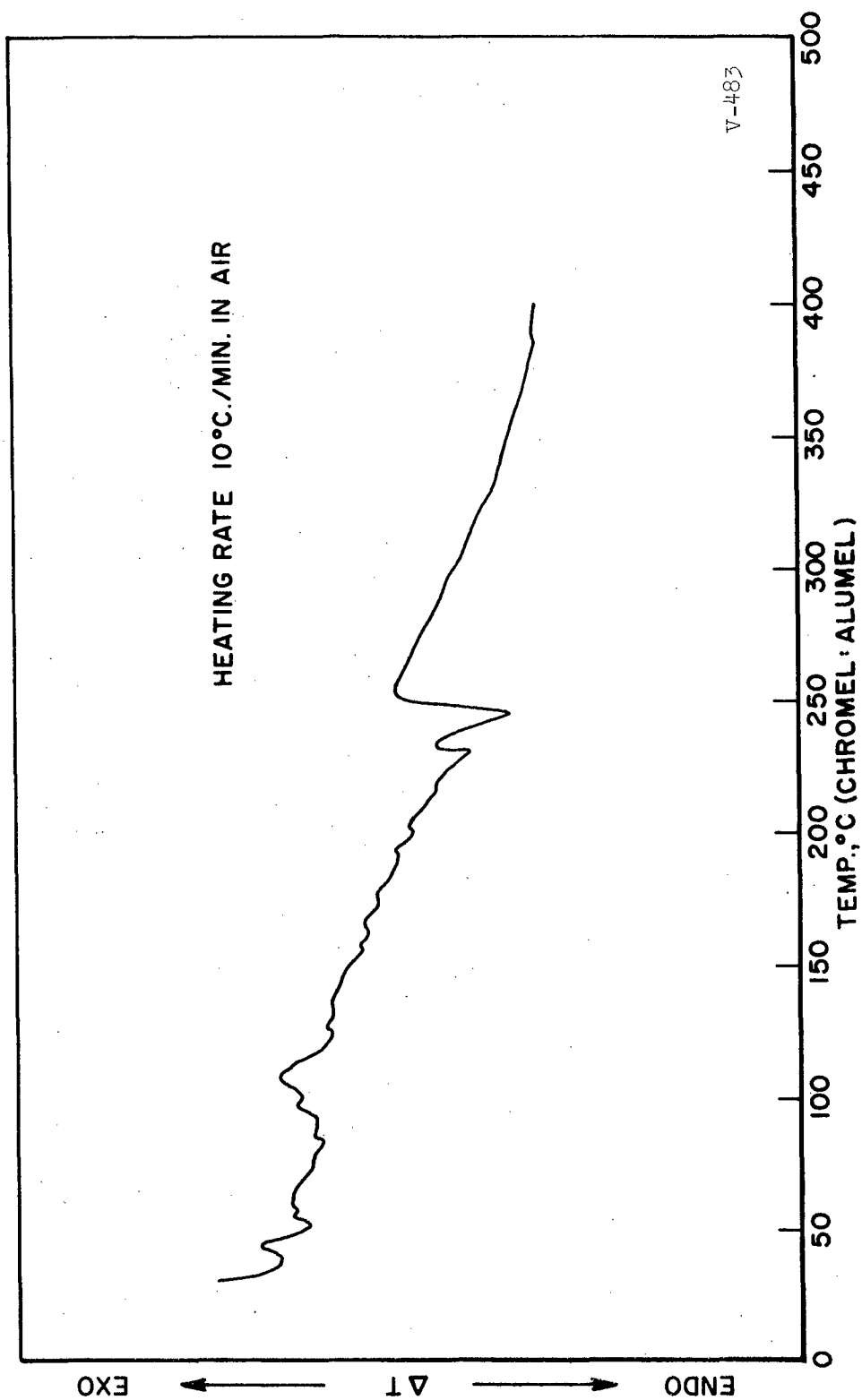


Fig. 4 - DTA of Polymer 119 in Air

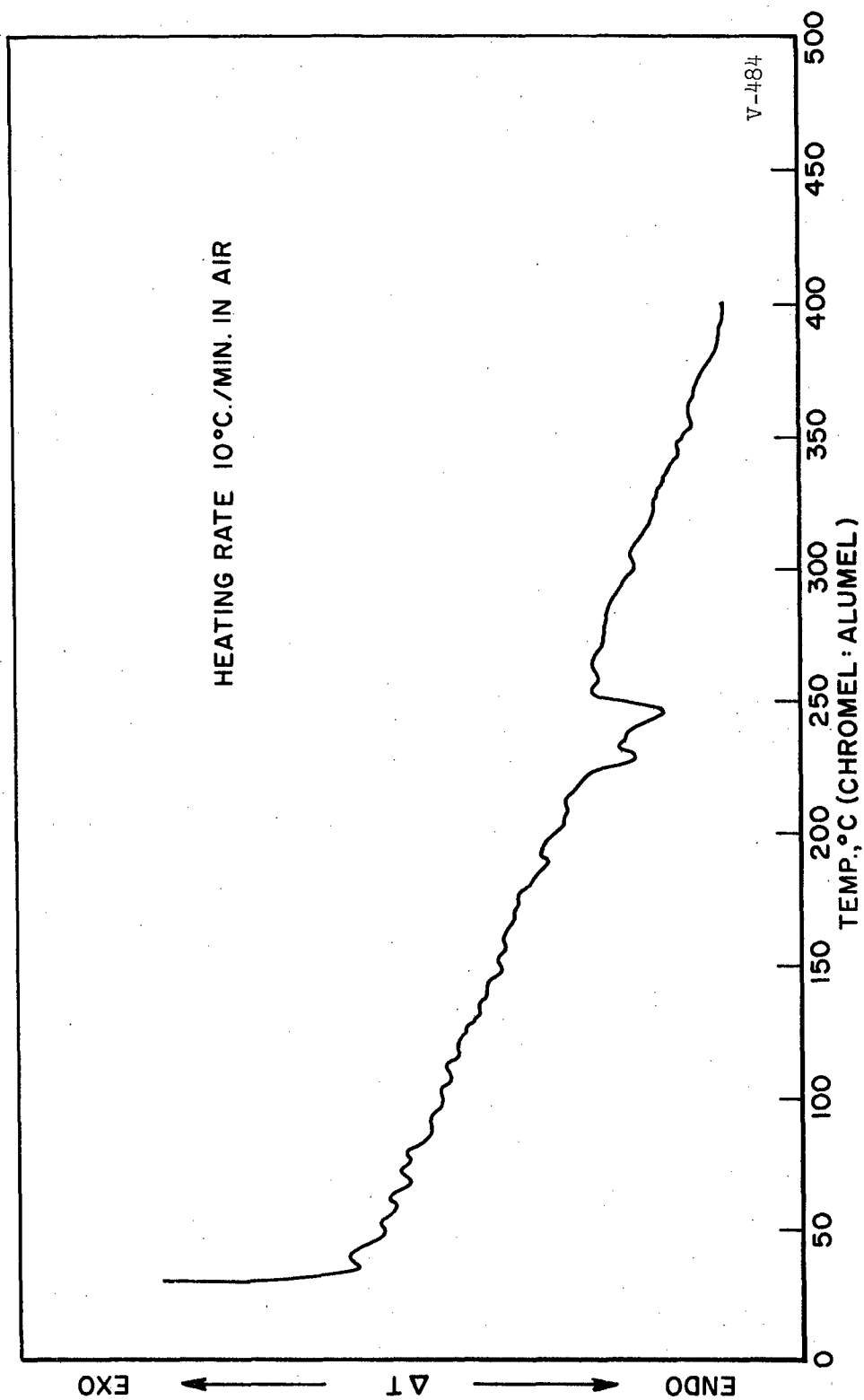


Fig. 5 - DTA of Polymer 119H in Air

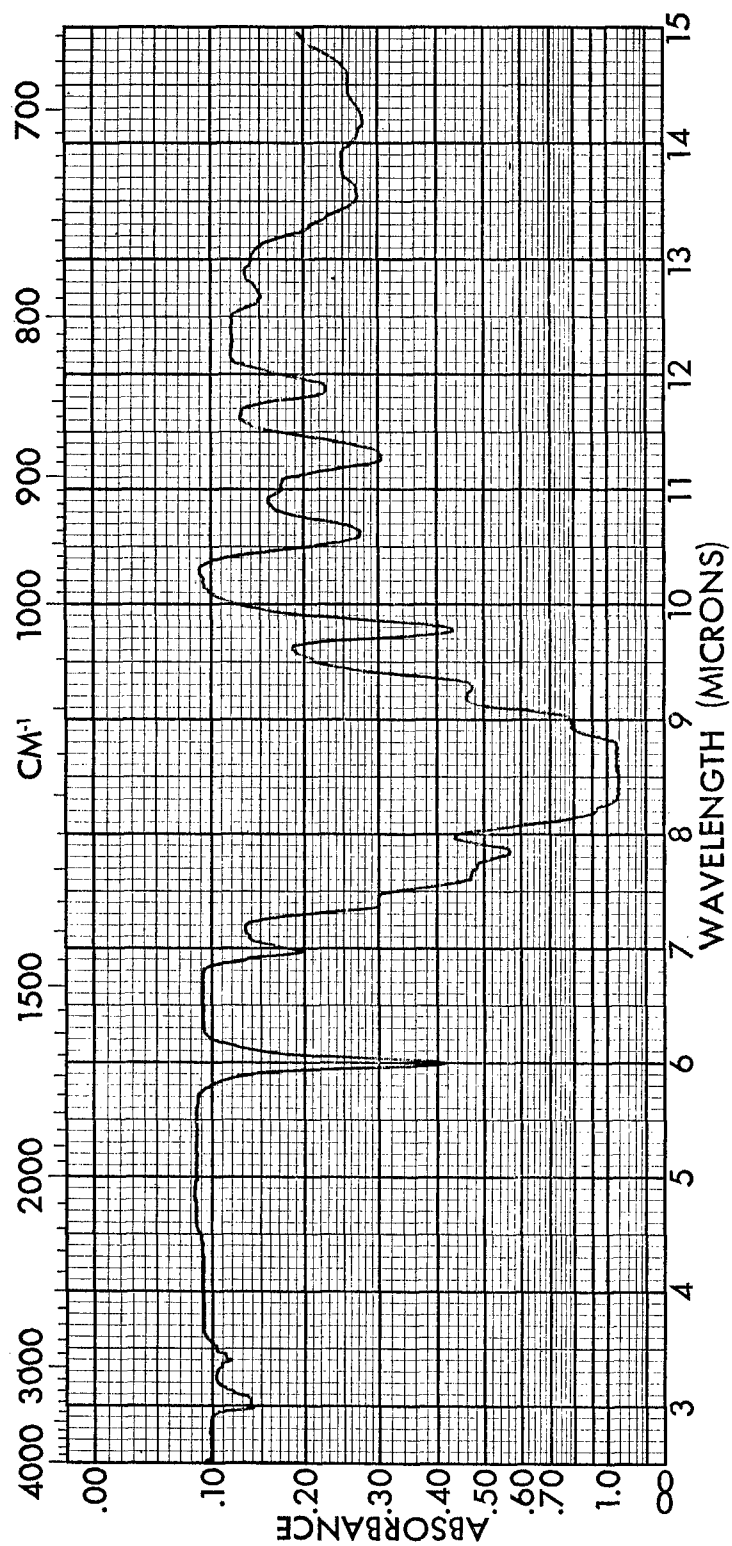


Fig. 6 - Infrared Spectrum of Dimethyl Perfluoro-4,9,14,19-Tetraoxadocosanedimide

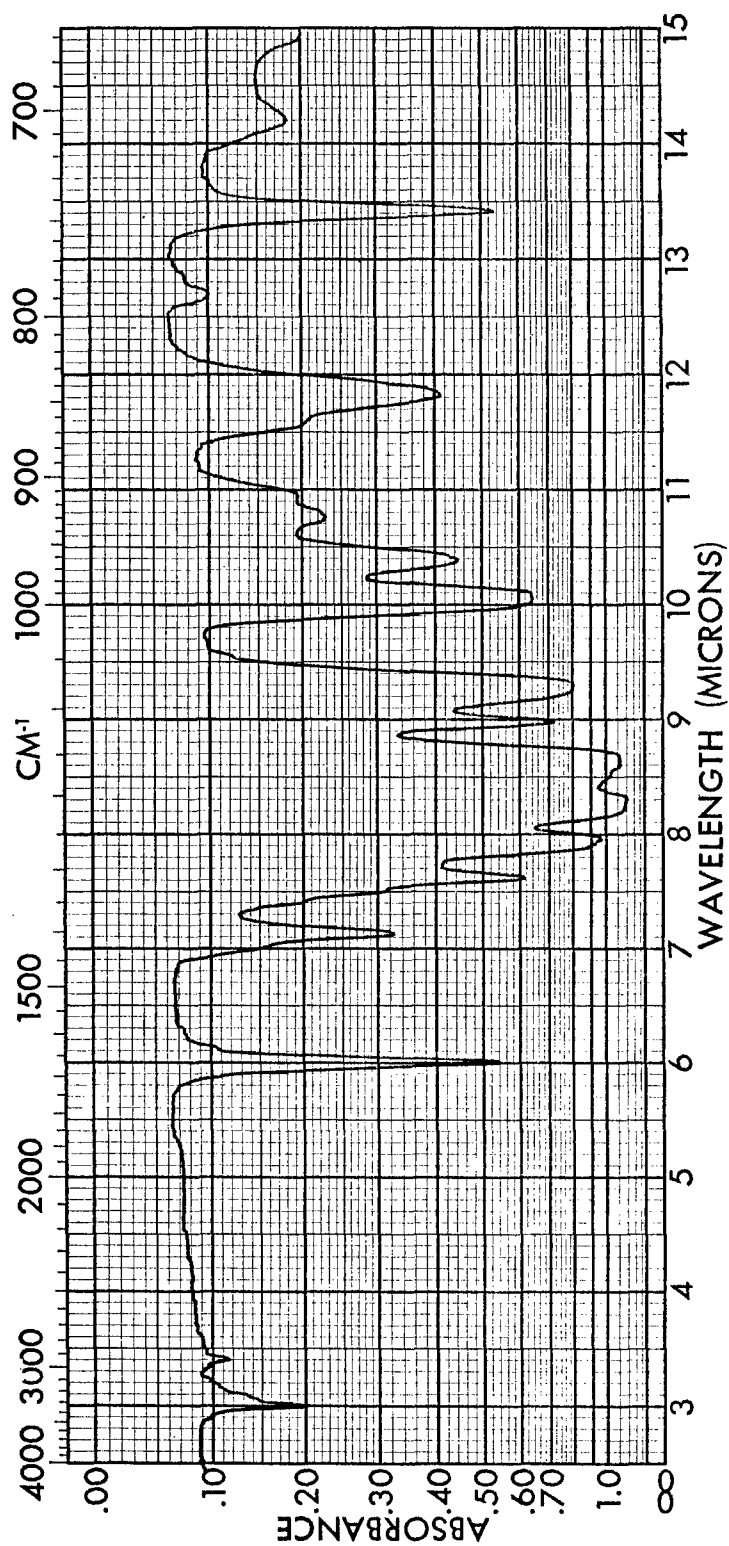


Fig. 7 - Infrared Spectrum of Trifluoroethyl Perfluorobutyrimide

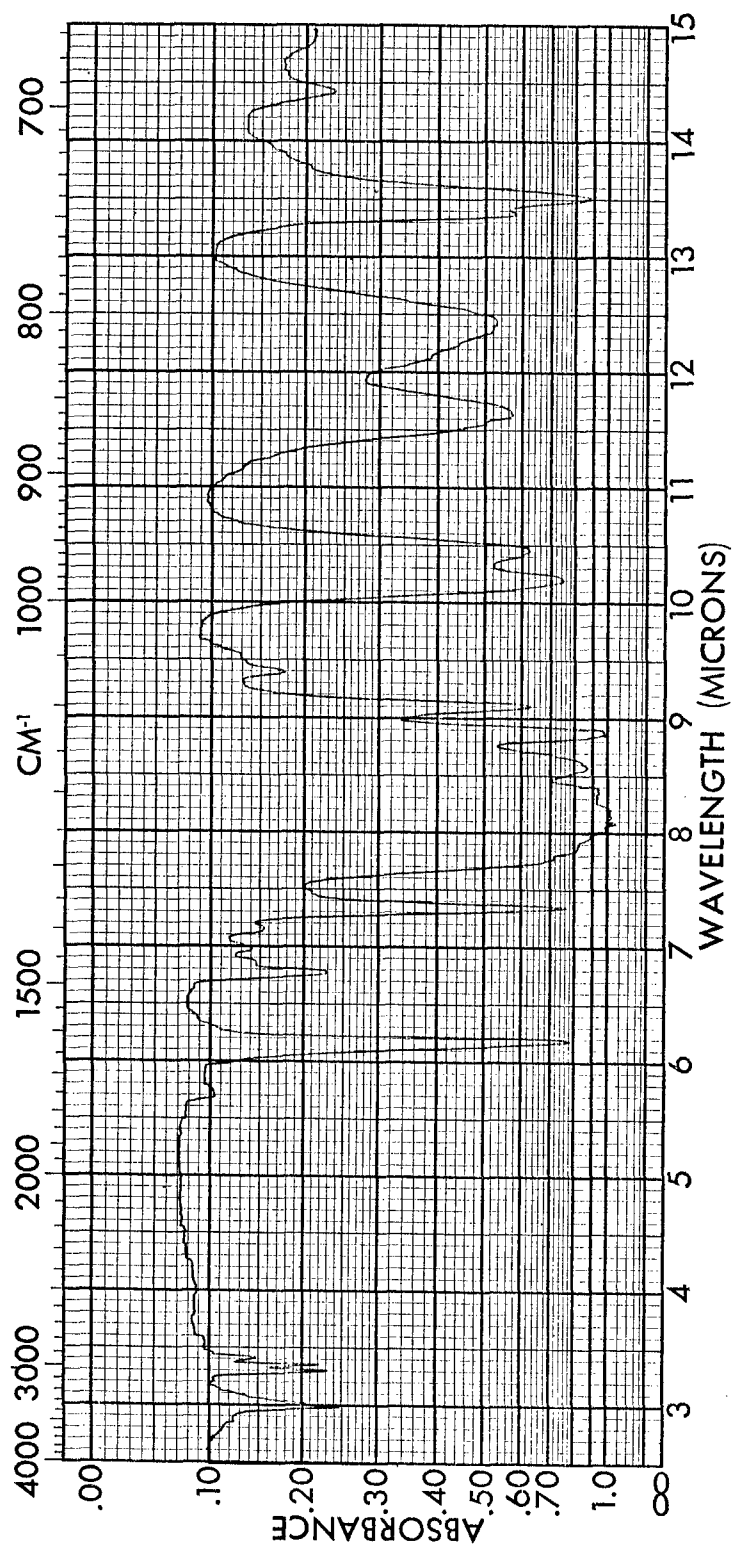


Fig. 8 - Infrared Spectrum of Ethyl Perfluorobutyrylthioimide

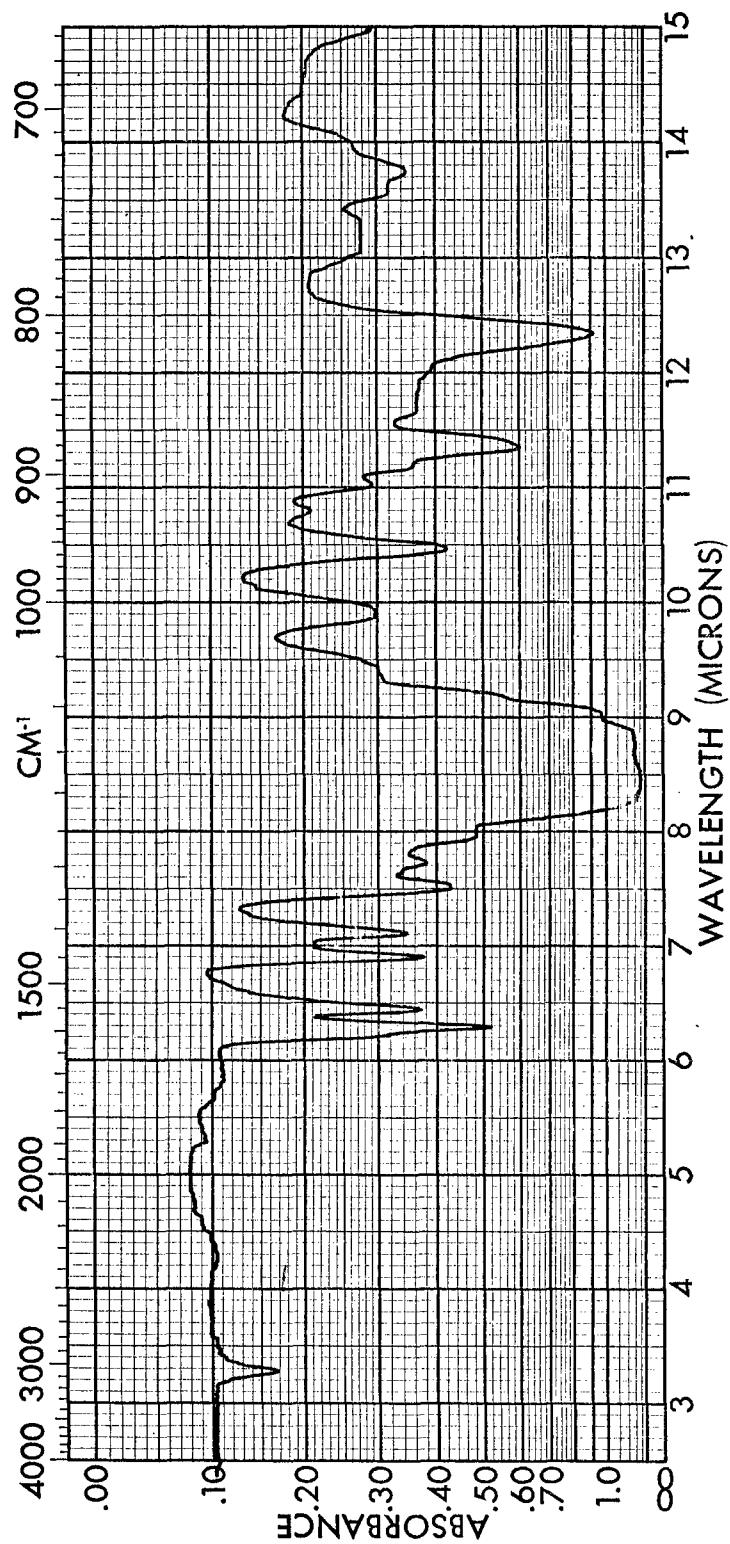


Fig. 9 - Infrared Spectrum of Perfluorosebacimide - Dihydroxybenzidine Copolymer Film

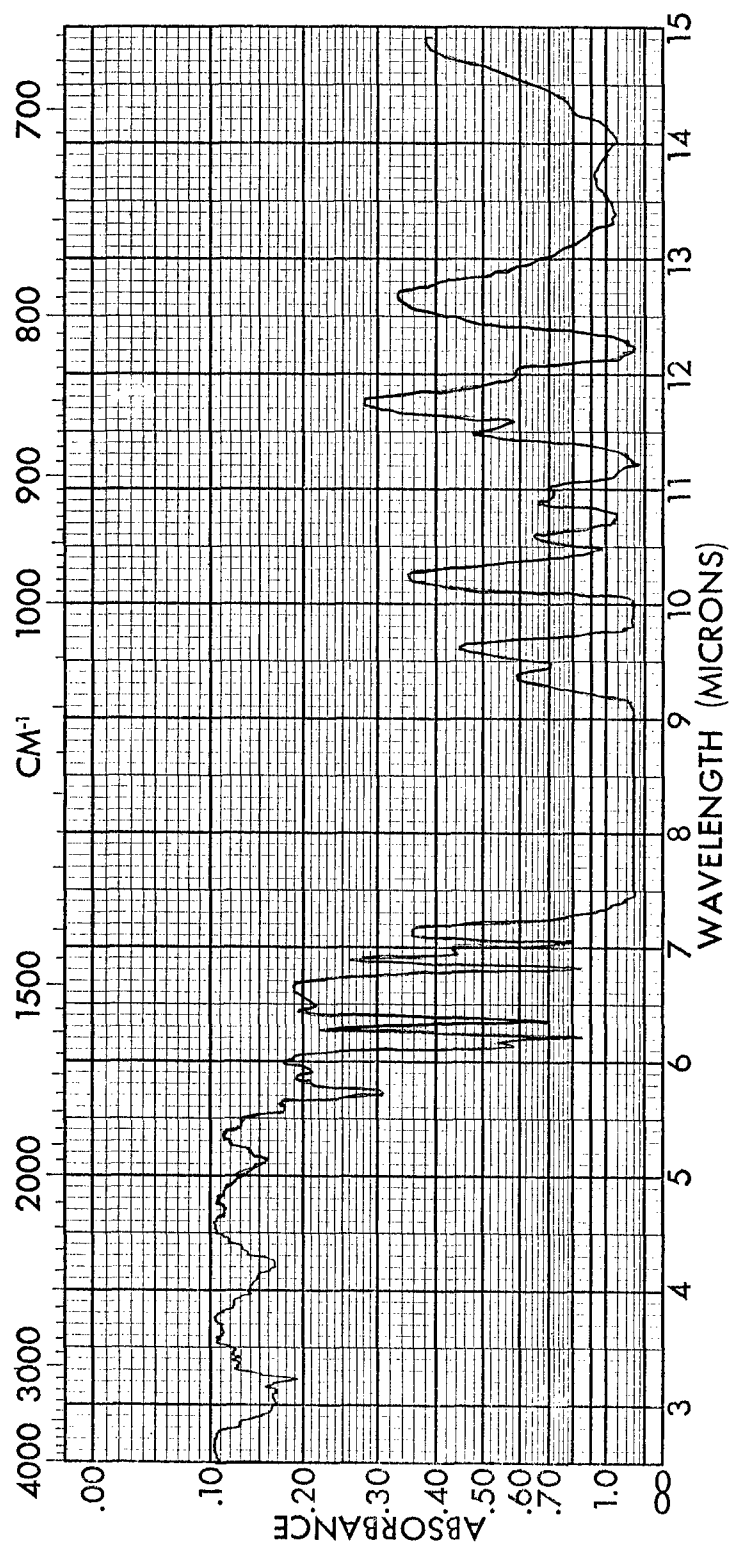


Fig. 10 - Infrared Spectrum of Perfluoro-4,9,14,19-Tetraoxadocosanedimide-Dihydroxybenzidine Copolymer

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1 ORIGINATING ACTIVITY (Corporate author) The Dow Chemical Company Midland, Michigan		2a. REPORT SECURITY CLASSIFICATION Unclassified	
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3 REPORT TITLE Synthesis and Characterization of Perfluoroalkyl Heterocyclic Elastomers			
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5 AUTHOR(S) (Last name, first name, initial) Madison, Norman L.; Burton, Charles D.			
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10 AVAILABILITY LIMITATION NOTICES This document is subject to special export controls and each transmittal to foreign government or foreign nationals may be made only with prior approval of the Polymer Branch, MANP, Nonmetallic Materials Div., Air Force Laboratory, WPAFB, Ohio.			
11. SUPPLEMENTARY NOTES		12 SPONSORING MILITARY ACTIVITY Non-metallic Materials Division Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433	
13 ABSTRACT Perfluoroalkyl bibenzoxazole polymers containing a $(CF_2)_8$ between heterocyclic rings have been prepared by the reaction of dihydroxybenzidine and methyl perfluorosebacimide. Through preparation of this polymer, the basic polymerization system has been significantly improved and polymers with number average molecular weights as high as 20,400 have been obtained in good yield and purity. These materials are thermally stable to $\sim 500^\circ C$. (TGA). Copolymers of dihydroxybenzidine and methyl perfluoro-4,9,14,19-tetraoxadocosanediimide, which are tacky and resilient, have been prepared by the same basic reaction. Number average molecular weights of $\sim 11,500$ have been achieved, but the polymer molecular weights have not been optimized. Thermal stability is comparable to the sebacimide polymer. Distribution has been made in accordance with the list supplied by the Air Force Materials Laboratory and is published at the back of this document.			

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal stable elastomers						
Perfluoroalkyl heterocyclics						
Perfluoroalkyl bibenzoxazole polymers						
Methyl perfluorosebacimide - dihydroxybenzidine copolymers						
Methyl perfluoro,4,9,14,19-tetraoxadocosanediimide-dihydroxybenzidine copolymers						

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